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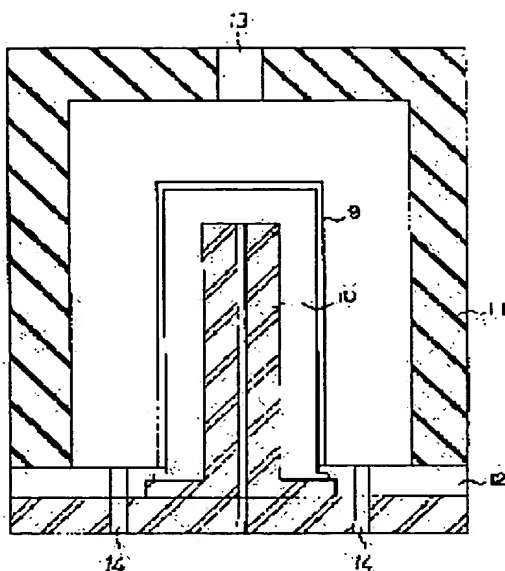
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(54) METHOD FOR FORMING SILICON OXIDE FILM OF UNIFORM FILM THICKNESS
ON THREE-DIMENSIONAL CONTAINER MADE OF PLASTIC MATERIAL



(57)Abstract:

PURPOSE: To coat a container with a transparent and uniform film superior in gas barrier properties by a method wherein an earth electrode is disposed over a film-forming surface of a container so that a distance between the surface of the container and the surface of the electrode is substantially constant and larger than a distance between a high-frequency electrode and the film-forming surface of the container, and a silicon oxide is deposited under specific conditions.

CONSTITUTION: When a film is applied to an outer surface of a container 9, a distance between a high-frequency electrode 10 and a

film-forming surface of a container 9 is determined to 10mm or less, and a distance between an earth electrode 11 and the film-forming surface of the container 9 is constant and larger than the distance between the film-forming surface and the high-frequency electrode 10. A silicon oxide film is deposited with a uniform film thickness on the surface of the container 9 opposed to the earth electrode 11 under a discharge gas pressure of 0.0005–0.05-torr by introducing a plasma of a silicon oxide generated by a CVD method into between the container 9 and the earth electrode 11. In this manner, a uniform film of such an ultra-precise film thickness as to have, for example, a film thickness difference of 200 μ m or less is formed on the container 9 of a three-dimensional structure for remarkably improving gas barrier properties.

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CLAIMS

[Claim(s)]

[Claim 1] The distance of the front face and electrode surface which form the coat of a container in the front-face side which does not form the coat of the container of a solid configuration with which T.g. consists of a high plastics ingredient from the film production temperature of a silicon oxide thin film arranges an almost fixed RF electrode by 10mm or less. A ground electrode with a distance of the front face of a container and an electrode surface large almost more fixed than the distance on an RF electrode and the front face of a container which forms a coat is installed in the front-face side which forms a coat. The plasma of the silicon oxide generated with the CVD method between a container and a ground electrode How to cover the silicon oxide thin film which was excellent in the container of the solid configuration which consists of a plastics ingredient characterized by making a silicon oxide thin film adhere to the front face which introduced and countered with the ground electrode of a container by discharge gas pressure 0.0005 – 0.05torr at the thickness of homogeneity at gas cutoff nature.

[Claim 2] The approach the distance of a container front face and a ground electrode covers with 11–100mm the silicon oxide thin film which was excellent in the container of the solid configuration which consists of an almost fixed plastics ingredient

indicated by claim 1 at gas cutoff nature.

[Claim 3] How to cover the silicon oxide thin film which was excellent in the container of a solid configuration with which a ground electrode consists of a plastics ingredient which are a container covering surface and one electrode which has the opposite front face of the same configuration mostly, and which was indicated by claims 1 or 2 at gas cutoff nature.

[Claim 4] How to cover the silicon oxide thin film which was excellent in the container of a solid configuration with which an RF electrode consists of a plastics ingredient indicated by claim 1 thru/or any 1 term of 3 which is the covering surface of a container, and one electrode which has the inner surface of the same configuration mostly at gas cutoff nature.

[Claim 5] The approach the silicon oxide thin film formed in the front face of the container of the solid configuration which consists of a plastics ingredient covers [thickness] with refractive indexes 1.4–1.5 the silicon oxide thin film which was excellent in the container of the solid configuration which consists of a plastics ingredient indicated by claim 1 thru/or any 1 term of 4 which is 300–2000Å at gas cutoff nature.

[Claim 6] The distance of the front face and electrode surface which form the coat of a container in the front-face side which does not form the coat of the container of a solid configuration with which T.g. consists of a high plastics ingredient from the film production temperature of a silicon oxide thin film arranges an almost fixed RF electrode by 10mm or less. A ground electrode with a distance of the front face of a container and an electrode surface large almost more fixed than the distance on an RF electrode and the front face of a container which forms a coat is installed in the front-face side which forms a coat. The organic silicon compound which consists of silicon, oxygen, and carbon at least by the low-temperature plasma method The plasma and nothing, Introduce this plasma between a container and a ground electrode, carry out a polymerization by discharge-gas-pressure 3×10^{-3} – 3×10^{-2} torr, and a silicon compound polymer thin film is formed in a container inner surface. With subsequently, a CVD method How to cover the silicon oxide thin film which was excellent in the container of the solid configuration which consists of a plastics ingredient characterized by supplying the plasma of the generated silicon oxide and forming the coat of a silicon oxide on a silicon compound thin film by discharge gas pressure 0.0005 – 0.05 torr at gas cutoff nature.

[Claim 7] The approach a silicon compound coat covers [thickness / those with 0.005 micrometers – 0.05 micrometer, and a silicon oxide coat] with refractive indexes

2.0-2.3 the silicon oxide thin film which was excellent in the container of the solid configuration which consists of a plastics ingredient whose thickness is 300-2000Å, and which was indicated by claim 6 at gas cutoff nature with refractive indexes 1.4-1.5.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the approach of covering the thin film of the transparent silicon compound which was excellent in the container which consists of a plastics ingredient used for a package at gas cutoff nature.

[0002]

[Description of the Prior Art] A packing material needs to prevent transparency of gas for protection of contents, and preservation, and the attempt of the conventional versatility is made. For example, prepare inorganic enveloping layers, such as silicon oxide and aluminum oxide, the laminating of the gas cutoff nature resin layers, such as a polyvinylidene chloride, is carried out, or to carry out the laminating of the metal film of aluminum foil has been tried. In addition, the laminated film which covered the synthetic resin same on a plastics film as the plastics with the shape of a thin film by vacuum deposition and sputtering to JP,3-183759,A, formed the organic layer, vapor-deposited the inorganic substance, formed the mixing layer of the organic substance and an inorganic substance on it, and formed the inorganic layer on it further is shown. In order for the inorganic substance of an enveloping layer to be completely different matter, for these plastics to cover the same synthetic resin as plastics in the shape of a thin film since compatibility is scarce, and to improve fixable [of an inorganic coat], the blend layer of synthetic resin and an inorganic substance is formed in the medium, but since, as for the front face of a blend layer, not the field of only an inorganic substance but the field of synthetic resin exists, fixable [of an inorganic layer] does not improve to the expected degree. Moreover, it is inapplicable to the Plastic solid except a sheet-like object to vapor-deposit synthetic resin and an inorganic substance at two processes. Furthermore, since molecular weight will fall if synthetic resin is vapor-deposited, as for the container which consists of this plastics ingredient, workability deteriorates. this invention person applied for JP,5-345383,A invention and Japanese-Patent-Application-No. No. 224903 [five to] invention

previously. Invention of this etc. is epoch-making invention from which the conventional packing material completely differs, and the fault of the conventional packing material was solved. However, although the coat of the thickness of homogeneity could be formed about the container which has three-dimensional structure, there was a little inadequate point in forming the coat of the thickness of ultraprecise homogeneity. And ultraprecise thickness is required of the package of a special application, for example, a special chemical etc.

[0003]

[Problem(s) to be Solved by the Invention] In the container of three-dimensional structure, the difference of thickness forms the coat of ultraprecise thickness 200Å or less, and this invention solves the problem of the above-mentioned thickness ununiformity, and carries out improvement in ***** of the gas cutoff nature.

[0004]

[The means which solved the technical problem] "This invention, the distance of the front face and electrode surface which form the coat of a container in the front-face side which does not form the coat of the container of a solid configuration with which T.g. consists of a high plastics ingredient from the film production temperature of a 1. Silicon oxide thin film arranges an almost fixed RF electrode by 10mm or less. A ground electrode with a distance of the front face of a container and an electrode surface large almost more fixed than the distance on an RF electrode and the front face of a container which forms a coat is installed in the front-face side which forms a coat. The plasma of the silicon oxide generated with the CVD method between a container and a ground electrode How to cover the silicon oxide thin film which was excellent in the container of the solid configuration which consists of a plastics ingredient characterized by making a silicon oxide thin film adhere to the front face which introduced and countered with the ground electrode of a container by discharge gas pressure 0.0005 – 0.05torr at the thickness of homogeneity at gas cutoff nature.

2. Approach distance of container front face and ground electrode covers with 11–100mm silicon oxide thin film which was excellent in container of solid configuration which consists of plastics ingredient indicated by the 1st almost fixed term at gas cutoff nature.
3. How to cover silicon oxide thin film which was excellent in container of solid configuration with which ground electrode consists of plastics ingredient indicated by container covering surface, the 1st term which is one electrode which has opposite front face of the same configuration mostly, or the 2nd term at gas cutoff nature.
4. How to cover silicon oxide thin film which was excellent in container of solid

configuration with which RF electrode consists of plastics ingredient indicated by any 1 term of covering surface of container, the 1st term which is one electrode which has inner surface of the same configuration mostly, or the 3rd term at gas cutoff nature.

5. Approach silicon oxide thin film formed in front face of container of solid configuration which consists of plastics ingredient covers [thickness] with refractive indexes 1.4–1.5 silicon oxide thin film which was excellent in container of solid configuration which consists of plastics ingredient indicated by any 1 term of the 1st term which is 300–2000Å thru/or the 4th term at gas cutoff nature.

6. Distance of Front Face and Electrode Surface Which Form Coat of Container in Front-Face Side Which Does Not Form Coat of Container of Solid Configuration with which T.G. Consists of a High Plastics Ingredient from Film Production Temperature of Silicon Oxide Thin Film Arranges Almost Fixed RF Electrode by 10mm or Less. A ground electrode with a distance of the front face of a container and an electrode surface large almost more fixed than the distance on an RF electrode and the front face of a container which forms a coat is installed in the front-face side which forms a coat. The organic silicon compound which consists of silicon, oxygen, and carbon at least by the low-temperature plasma method The plasma and nothing, Introduce this plasma between a container and a ground electrode, carry out a polymerization by discharge-gas-pressure 3×10^{-3} – 3×10^{-2} torr, and a silicon compound polymer thin film is formed in a container inner surface. With subsequently, a CVD method How to cover the silicon oxide thin film which was excellent in the container of the solid configuration which consists of a plastics ingredient characterized by supplying the plasma of the generated silicon oxide and forming the coat of a silicon oxide on a silicon compound thin film by discharge gas pressure 0.0005 – 0.05 torr at gas cutoff nature.

7. approach a silicon compound coat covers [thickness / those with 0.005 micrometers – 0.05 micrometer, and a silicon oxide coat] with refractive indexes 2.0–2.3 the silicon oxide thin film which was excellent in the container of the solid configuration which consists of a plastics ingredient whose thickness is 300–2000Å, and which was indicated by the 6th term at gas cutoff nature with refractive indexes 1.4–1.5. ” -- it is related.

[0005]

[Function] the 1st description which does a special operation of this invention so is having arranged the external electrode which surrounded the container to the exterior of the container of a solid configuration, and the distance of the outside surface of a container and an external electrode surface being about 1 law, and having arranged

inside a container the internal electrode whose distance of the inner surface of a container and an electrode surface is about 1 law. Furthermore, it is the description that the distance of the front face of an external electrode and a container inner surface is 10mm or less when covering a thin film to the inner surface of a container, and the distance of the front face of an internal electrode and a container outside surface is 10mm or less when covering a thin film on the outside surface of a container. The distance on an electrode and the front face of a container is kept constant for setting field strength distribution constant. The distance of an RF electrode and the front face in which the coat of a container is prepared must be 10mm or less. It is because the problem to which the gas cutoff nature of a coat falls rapidly when it comes to 10mm or more arises. Moreover, the distance on a ground electrode and the front face of a coat of a container must be larger than the distance of the field and RF electrode which prepare a coat. The discharge stabilized when the front face in which the coat of a container is prepared, the distance of an RF electrode, and the distance of the front face in which the coat of a container is prepared, and a ground electrode were equal is not obtained. And on the discharge conditions of this invention, discharge discharges in the one where the distance on an electrode and the front face of a container is larger. So, in this invention, enlarge distance of a container front face and a ground electrode, it is made to discharge between them, and a coat is formed. The distance on a ground electrode and the front face of a container is 11–100mm preferably, and is 11–70mm preferably.

[0006] The 2nd description of this invention is using one ground electrode and one RF electrode. The thickness of the coat which becomes fixed [the intensity distribution of electric field] to a precision, and is formed serves as homogeneity by using such two electrodes together.

[0007] The plasma of a silicon oxide is made to generate using a CVD method, by 0.0005 or less torrs, a film production rate falls [discharge gas pressure] extremely, the 3rd description of this invention is in the condition which cannot carry out real film production, and the problem to which the gas cutoff nature of a coat falls [gas pressure] rapidly by 0.05 or more torrs produces it.

[0008] The 4th description of this invention is using the container which T.g.'s formed with the high plastics ingredient from the film production temperature of silicon oxide thin ** as a container which covers. It is because deformation of a container must be avoided at the time of film production in order to form an ultraprecise thin film. Such 1st description – the 4th description are put together, and the plasma of a silicon oxide is introduced between an electrode surface and a container wall. Since field

strength distribution in the meantime is fixed, plasma concentration becomes fixed, and on a container wall, a silicon oxide deposits and is covered with uniform thickness. In this way, the silicon oxide coat of fixed thickness is formed.

[0009] The number of internal electrode and external electrodes must also be one, respectively, and using two or more electrodes must avoid. If two or more electrodes are used, a uniform coat cannot be formed even if it uses a CVD method. this invention person studied [why a uniform coat is not formed and] many things. For example, as shown in drawing 3 , two or more electrodes have been arranged so that distance with the outside surface of a container may become fixed, and when the silicon oxide was covered with the CVD method, the thickness of a coat did not become fixed as the next example of a comparison showed. Although thickness became homogeneity when it covered rotating a container at a fixed rate furthermore, the gas cutoff nature of the covered film did not improve. Since the field strength distribution which each electrode has since two or more electrodes were used interferes mutually, it influences, the concentration of the plasma changes and this invention person is the mixture of the film formed of different field strength when thickness did not become homogeneity and a container was rotated, he thinks that the film excellent in gas cutoff nature is not formed.

[0010] Although this invention uses a CVD method, the CVD method using a RF, an alternating current, and a direct current etc. is used. A refractive index is [the thickness of the silicon oxide coat formed of this invention] 300–2000Å in 1.4–1.5. By 300Å or less, the continuation film is not obtained for thickness, gas cutoff nature does not improve, and even if it covers 2000Å or more, improvement in gas cutoff nature is seldom found, but the problem which the film destroys with internal stress conversely arises. As for the ingredient used in order to form the silicon oxide plasma with a CVD method by this invention, helium, Ar gas, etc. are used as organosilicon compounds, such as SiH_4 , NO_x gas, oxygen gas, TEOS (tetra-ethoxy silane), and HMDSO (hexa methyl disiloxane), NO_x , oxygen gas, and plasma auxiliary gas. Thus, the formed silicon oxide coat is the container which did the outstanding gas screening effect so and was dramatically excellent in the usual application.

[0011] The 5th description of this invention can be covered to both of the fields by choosing whether a ground electrode is arranged to the inner surface side of a container, or it arranges to an outside surface side. Moreover, inside-and-outside both sides can also be covered by changing the location of a ground electrode and carrying out two or more times.

[0012] The silicon compounds used for forming a silicon oxide coat by this invention

are liquefied monomers, such as a silane, and a vinyl ethoxy silane, phenyltrimethoxysilane.

[0013] This invention to the side which does not form the coat of the container of the solid configuration which consists of a plastics ingredient with T.g. higher than the film production temperature of a silicon oxide thin film again The distance of the front face and electrode surface in which the coat of a container is prepared installs an almost fixed RF electrode by 10mm or less. Moreover, to the side which forms the coat of a container, the distance of a container front face and an electrode surface arranges an RF electrode and a ground electrode large almost more fixed than the distance on the front face of a container. The organic silicon compound which consists of silicon, oxygen, and carbon at least by the low-temperature plasma method The plasma and nothing, Supply this plasma between a container front face and a ground electrode, carry out a polymerization by gas pressure 3×10^{-3} – 3×10^{-2} torr, and a silicon compound polymer thin film is formed in a container inner surface. With subsequently, a CVD method The approach of forming the silicon oxide coat of the thickness of homogeneity in the container which consists of a plastics ingredient characterized by supplying the plasma of the generated silicon oxide and discharge forming the coat of a silicon oxide on a silicon compound thin film by gas pressure 0.0005 – 0.05 torr is also included. While the coat which consists of this bilayer is excellent in gas cutoff nature, the amount of steam transparency does so the very high steam screening effect not more than 0.1 g/m²day. If a ground electrode and an RF electrode are arranged and this silicon compound polymer coat and a silicon oxide coat are formed, since a uniform coat is formed, gas cutoff nature of both coats will improve remarkably.

[0014] Although that academic break through is not necessarily enough in why such special effectiveness will be done so if the laminating of two sorts of these layers is carried out in this sequence, this invention does so the operation effectiveness which carries out a repetitive rendering. this invention person thinks that ***** is large with the gas screening effect of a silicon oxide layer being based on the stable fixable one of the silicon oxide particle supplied on a coat base. That is, the supplied particle moves in a plastics base top, is stabilized and is established in the most stable location. In this case, if the polymer coat of the silicon compound containing silicon, carbon, and oxygen is formed on the plastics base, a silicon oxide particle will be stabilized good and will be established. And I think that it is because the distribution becomes uniform, a silicon oxide particle is piled up further and a silicon oxide coat is formed on the stable silicon oxide particle, so it becomes a close coat.

[0015] Moreover, I think that it is because it will become few close coats of the defect

in which fixable is more high, about the super-steam gas cutoff nature not more than 0.1 g/m²day being shown if the silicon compound polymer coat of the first pass and the silicon oxide coat of the second layer are within the limits of a specific refractive index, respectively.

[0016] In the presentation of the silicon in the first pass, carbon, and oxygen, 15% or more of silicon, 20% or more of carbon, and the remainder contain oxygen, and the 1st organosilicon compound polymer enveloping layer is a 0.005 micrometers – 0.05 micrometers film. If the thickness of an enveloping layer becomes thicker than this, gas cutoff nature will worsen.

[0017] The special organosilicon compound polymer coat of such the first pass can plasma-ize organosilicon compound monomers, such as for example, hexa methyl disiloxane, and can form them by carrying out a polymerization on a plastics base. The refractive index of the coat formed by adjusting the gas pressure at the time of this polymerization to 3×10^{-3} to 3×10^{-2} torr can be set to 2.0–2.3. Conventionally, although it is other applications, since discharge gas pressure is the range of 0. number torr to number +torr, the plasma-CVD method learned is understood that the plasma-CVD method used by this invention is special.

[0018] As an organic silicon compound monomer used by this invention, they are vinyltriethoxysilane, vinyltrimetoxysilane, a tetramethoxy silane, a tetra-ethoxy silane, phenyltrimethoxysilane, octamethylcyclotetrasiloxane, methyl trimetoxysilane, methyl triethoxysilane, 1133-tetramethyl disiloxane, hexane methyl disiloxane, etc. Compounds, such as this, are used also for formation of a **** oxide coat.

[0019]

[Example] An example is given and it is explained that this invention is intelligible.

[0020] Example 1 drawing 1 is an RF plasma CVD system which forms the organic silicon compound coat used by this invention. This equipment consists of fixture 8 grade for samples installed between the cylindrical ground electrodes 2 and two electrodes with the bell jar mold vacuum chamber 1 made from stainless steel with an equipped with the inlet 6 and the oxygen gas inlet 7 which introduce a silane and an ordinary temperature liquid monomer by the gaseous state diameter of 60cm, the JEOL Co., Ltd. make and RF generator 5, a matching box [4] and disc-like RF electrode 3 with a diameter of 13cm, a diameter [of 20cm, and a height of 1.5cm. The equipment of this drawing 1 can perform both an organosilicon compound coat and the coat of the silicon oxide film which is a gas filter layer. a vacuum pump should use an oil sealed rotary pump and an oil diffusion pump, and should always continue a pump during pretreatment and membrane formation -- pretreatment and a thin film coat

trial were performed. As an ordinary temperature liquid monomer, oxygen gas was used as hexa methyl disiloxane (it is described as Following HMDSO), and reactant gas. It is introduced in a chamber by another root, and is mixed within a ground electrode, and these gas is emitted in a chamber, respectively. The ground electrode and the RF electrode have been arranged to parallel (distance of 70mm), and installed the 100micro polycarbonate (it is described as Following PC) sheet in the RF electrode and the ground electrode (it is 5mm from an RF electrode) with the insulating sample fixture as a sample. The degree of vacuum in a chamber was lengthened to the vacuum to $2 - 3 \times 10^{-5}$ torr (ionization vacuum gage) with the oil sealed rotary pump and the oil diffusion pump, oxygen gas was introduced and it continued until the degree of vacuum in a chamber was set to 1×10^{-3} torr, and the HMDSO steam was introduced until the degree of vacuum in a chamber was set to 2×10^{-3} torr. From the RF generator, incidence power 200W were introduced in the chamber via the matching box, the mixed plasma of oxygen and HMDSO was generated, it held for 10 minutes, and oxidation silicon **** was formed on PC sample. The amount of steam transparency of this layered product was measured with the amount measuring instrument of steam transparency made from Mocon, and was shown in a table 1.

[0021] Except having installed the location of the sample installed in example 2 and example of comparison 1 RF electrode, and ground inter-electrode in 3, 7, 9, 23, and 40mm on the RF substrate, it was the same conditions as an example 1, and oxidation silicon **** was formed on PC sample, the amount of steam transparency was measured, and it was shown in a table 1 with the example 1.

[0022]

[A table 1]

	高周波電極—基板 間距離 (mm)	水蒸気透過量 $\text{g}/\text{m}^2 \text{ day}$
実施例 1	5	0.07
実施例 2	0	0.10
	3	0.09
	7	0.07
	9	0.10
比較例 1	23	1.3
	40	3.1

[0023] Except that thickness used the -15 to 105 degrees C plastic sheet for example 3 and example of comparison 2 sample by 100micro–280micro, glass transition

temperature (it is described as Following T_g) is an example 1 and the same conditions, oxidation silicon **** was formed on the sample, the amount of steam transparency was measured, and it was shown in a table 2. As a result of measuring the temperature on the front face of a sample with an optical-fiber type thermometer, on this condition, it was 45 degrees C.

[0024]

[A table 2]

	基板のT _g (℃)	水蒸気透過量
実施例3	125	0.03
	115	0.04
	105	0.03
	97	0.04
	91	0.08
	67	0.1
比較例2	-10	0.4

[0025] Example 4 drawing 2 is the explanatory view showing the cross section of the electrode for a container outside surface coat used for this invention. Nine in drawing is a closed-end cylindrical shape [made from polyethylene terephthalate (henceforth, PET)]-like container. 10 is an internal RF electrode and the outside surface serves as the same configuration as the outside surface of a closed-end cylindrical shape-like container. And the distance of the outside surface of an electrode 10 and a container outside surface is fixed at about 5mm. 11 is an external ground electrode, the inner surface of an electrode 11 is the almost same configuration as the outside surface of the closed-end cylindrical cup 9, and both distance is almost fixed at about 12mm. The ground electrode 11 and RF electrode 10 are arranged through the insulator 12, a gas inlet 13 is installed in the upper part of the ground electrode 11, and the flueing opening 14 is installed in the lower part of the electrode for a container outside surface coat again. From a gas inlet 13, reactant gas and monomer gas are introduced in an electrode, are plasma-ized, flow along the outside surface of the closed-end cylindrical shape-like container 9, and are exhausted out of an electrode from the flueing opening 14. A silicon oxide coat is formed in the outside surface of the closed-end cylindrical shape-like container 9 in this electrode. With the electrode for a container outside surface coat which has arranged the closed-end cylindrical shape-like container 9, the equipment shown in drawing 1 was used and the silicon oxide coat was formed in the container outside surface. Formation of an oxidation

silicon object coat removed the fixture 8 for samples in drawing 1 , has arranged the electrode for a container outside surface coat of drawing 2 between the RF electrode 3 ground electrodes 2 in drawing 1 , and connected the ground electrode 11 of the cylindrical ground electrode 2 and the electrode for a container outside surface coat, and connected disc-like RF electrode 3 and RF electrode 10 for a container outside surface coat. The degree of vacuum in a chamber was lengthened to the vacuum to $2 - 3 \times 10^{-5}$ torr (ionization vacuum gage) with the oil sealed rotary pump and the oil diffusion pump, oxygen gas was introduced and it continued until the degree of vacuum in a chamber was set to 1×10^{-3} torr, and the HMDSO steam was introduced until the degree of vacuum in a chamber was set to 2×10^{-3} torr. From the RF generator, incidence power 200W were introduced in the chamber via the matching box, the mixed plasma of oxygen and HMDSO was generated, it held for 10 minutes, and oxidation silicon **** was formed in the outside surface of a closed-end cylindrical shape-like container. Oxidation silicon object thickness distribution of the drum section of a closed-end cylindrical shape-like container and the amount of steam transparency were measured, and it was shown in a table 3.

[0026] As shown in example of comparison 3 drawing 3 , it covered as the same conditions as an example 4 from the cylindrical shape-like container outside surface at the equal distance except having arranged four external RF electrodes 15 at the location which serves as equiangular [of 90 degrees] from a cylinder core on the outside of the same closed-end cylindrical shape-like container 9 as an example 4. Oxidation silicon object thickness distribution of the drum section of the closed-end cylindrical shape-like container 9 and the amount of steam transparency were measured, and it was shown in a table 3 with the example 4. Drawing 4 is the explanatory view which saw the coat equipment of drawing 3 from the upper part, and measuring points 0D, 45D, and 90D are specified.

[0027] It covered as the same conditions as the example 3 of a comparison except carrying out the axial revolution of the example of comparison 4 closed-end cylindrical shape-like container 1 by 4rpm. Oxidation silicon object thickness distribution of the drum section of the closed-end cylindrical shape-like container and the amount of steam transparency were measured, and it was shown in a table 3 with the example 4 and the example 3 of a comparison.

[0028]

[A table 3]

測定位置	膜厚 (A)			屈折率			水蒸気透過量 g/m ² day
	0D	45D	90D	0D	45D	90D	
実施例 4	950	980	930	1.45	1.47	1.44	0.02
比較例 3	510	1680	620	1.42	1.69	1.44	1.85
比較例 4	940	990	950	1.55	1.60	1.56	1.05

[0029] Example 5 drawing 5 is the explanatory view showing the cross section of the electrode for a container inner surface coat used for this invention. Nine in drawing is a cup configuration container made from an annular olefin copolymer (henceforth, COC). 15 is an external RF electrode and the internal surface serves as the same configuration as the inner surface of a cup configuration container. And the distance of the internal surface of an electrode 15 and a container internal surface is fixed at about 5mm. 16 is an internal ground electrode, the outside surface of an electrode 16 is the almost same configuration as the inner surface of the cup configuration container 9, and both distance is almost fixed at about 20mm. The ground electrode 16 and RF electrode 15 are arranged through the insulator 12, a gas inlet 13 is installed in the lower part of the ground electrode 16, and the flueing opening 14 is installed in the upper part of a ground electrode again. From a gas inlet 13, reactant gas and monomer gas are introduced in an electrode, are plasma-ized, flow in accordance with the inner surface of the cup configuration container 1, and are exhausted out of an electrode from the flueing opening 14. A silicon oxide coat is formed in the internal surface of the cup configuration container 9 in this electrode. With the electrode for a container inner surface coat which has arranged the cup configuration electrode, the equipment shown in drawing 1 was used and the silicon oxide coat was formed in the container internal surface. Formation of an oxidation silicon object coat removes the fixture 8 for samples in drawing, and arranges the electrode for a container inner surface coat of drawing 5 between RF electrode 3 in drawing 1, and the ground electrode 2. Connect the ground electrode 16 of the cylindrical ground electrode 2 and the electrode for a container inner surface coat, and connect disc-like RF electrode 3 and RF electrode 15 for a container inner surface coat, introduce SiH₄ gas from a monomer inlet, and oxygen is introduced from an oxygen gas inlet. These mixed-gas plasma was formed, by 3x10⁻³torr, the oxidation silicon film was deposited in the inner surface of a cup **-like container, and the discharge pressure was carried out to it. As a result of measuring the amount of steam transparency of the cup top container which covered the oxidation silicon film, it was 0.02 g/m²day (40-degree-C90%RH).

[0030] The closed-end cylindrical shape [made from example 6 polyethylenenaphthalate (it is described as Following PEN)]-like container was used, with the electrode for a container outside surface coat, the equipment shown in drawing 2 was used and the HMDSO polymer coat and the silicon oxide coat were formed in the container outside surface. The coat approach covered as the same conditions as an example 4 except the conditions described as a closed-end cylindrical shape-like container below. The degree of vacuum in a chamber was lengthened to the vacuum to $2 - 3 \times 10^{-5}$ torr (ionization vacuum gage) with the oil sealed rotary pump and the oil diffusion pump, and the HMDSO steam was introduced until the degree of vacuum in a chamber was set to 3×10^{-3} torr – 10×10^{-3} torr. From the RF generator, incidence power 400W were introduced into the chamber, the plasma of HMDSO was generated, it held for 1 minute, and the HMDSO polymer coat was formed in the outside surface of a closed-end cylindrical shape-like container. Then, the degree of vacuum in a chamber was lengthened to the vacuum to $2 - 3 \times 10^{-5}$ torr with the oil sealed rotary pump and the oil diffusion pump, and the coat of a silicon oxide was formed on the HMDSO polymerization film like the example 5. It was an ellipsometer about the refractive index of the film of the closed-end cylindrical shape-like container which covered these coats, and thickness, and with the weight method, the amount of steam transparency was measured and it was shown in a table 4.

[0031]

[A table 4]

	H M D S O		HMDSO膜		二層膜の水蒸気透過量
	濃 度	被覆時間	屈折率	膜厚	
実施例 6	3	0.5 分	2.05	60	0.04
	3	1.0 分	2.05	100	0.03
	3	2.0 分	2.05	210	0.05
	8	0.5 分	2.25	80	0.02
	8	1.0 分	2.25	150	0.02
	8	2.0 分	2.25	320	0.03
	10	0.5 分	2.04	120	0.05
	10	1.0 分	2.04	240	0.06
	10	2.0 分	2.04	480	0.08

[0032] (**) unit [of HMDSO concentration]; -- unit;g/m² of $\times 10^{-3}$ torr, the unit; angstrom of thickness, and the amount of steam transparency -- day and at 40-degree-C90%RH and [0033] Except the concentration of example of comparison

5HMDSO being [the coat time amount of 1.5×10^{-3} torr, 20×10^{-3} torr, and the HMDSO film] 0.2 and 5 minutes, the refractive index and thickness of the HMDSO film which were covered on the outside surface of the same closed-end cylindrical shape-like PEN container as an example 6 were measured by the ellipsometer, and the amount of steam transparency of the HMDSO film and a silicon oxidation cascade screen was measured with the weight method, and it was made a table 5.

[0034]

[A table 5]

	H M D S O		HMDSO膜		二層膜の
	濃 度	被覆時間	屈折率	膜厚	水蒸気透過量
比較例 5	2	0.2 分	1.76	30	0.15
	2	5 分	1.78	770	0.45
	20	0.5 分	1.68	300	0.32
	20	5 分	1.66	6000	0.47
未 被 覆					0.49

[0035] (**) unit [of the concentration of HMDSO]; -- unit:g/m² of the amount of steam transparency of the thickness; angstrom of 10^{-3} torr and the HMDSO film, and the bilayer film -- day and at 40-degree-C90%RH and [0036] The closed-end cylindrical shape [made from example 7 polyethylenenaphthalate (it is described as Following PEN)]-like container was used, with the electrode for a container outside surface coat, the equipment shown in drawing 2 was used and the HMDSO polymer coat and the silicon oxide coat were formed in the container outside surface. The coat approach covered as the same conditions as an example 4 except the conditions described as a closed-end cylindrical shape-like container below. The degree of vacuum in a chamber was lengthened to the vacuum to $2 - 3 \times 10^{-5}$ torr (ionization vacuum gage) with the oil sealed rotary pump and the oil diffusion pump, and the HMDSO steam was introduced until the degree of vacuum in a chamber was set to 4×10^{-3} torr. From the RF generator, incidence power 400W were introduced in the chamber, the plasma of HMDSO was generated, it held for 1 minute, and the HMDSO polymer coat was formed in the outside surface of a closed-end cylindrical shape-like container. Then, the degree of vacuum in a chamber was lengthened to the vacuum to $2 - 3 \times 10^{-5}$ torr with the oil sealed rotary pump and the oil diffusion pump, it is the range of 0.5-2.5 about the ratio of concentration (the ratio of the degree of vacuum in a chamber by the ionization vacuum gage; HMDSO/oxygen) of a HMDSO steam and oxygen, and the coat of a silicon oxide was formed for the coat time amount of the

oxidation silicon film on the HMDSO polymerization film like the example 5 except 5 – 20 minutes. It was an ellipsometer about the refractive index of the film of the closed-end cylindrical shape-like container which covered these coats, and thickness, and with the weight method, the amount of steam transparency was measured and it was shown in a table 6.

[0037]

[A table 6]

	HMDSO/O ₂ の比率	酸化珪素膜 の被覆時間	酸化珪素膜		二層膜の 水蒸気透過量
			屈折率	膜厚	
実施例 7	0.5	5.0	1.43	510	0.03
	0.5	10.0	1.44	1060	0.02
	0.5	20.0	1.44	1980	0.02
	1.0	5.0	1.45	490	0.02
	1.0	10.0	1.45	1080	0.02
	1.0	20.0	1.46	2010	0.02
	2.5	5.0	1.46	520	0.03
	2.5	10.0	1.46	1050	0.04
	2.5	20.0	1.46	2030	0.05

[0038] (**) unit;g/m² of the amount of steam transparency of the unit; angstrom of the thickness of a part for unit [of the coat time amount of the oxidation silicon film],, and the oxidation silicon film, and the bilayer film — day and at 40-degree-C90%RH and [0039] It is 0.5 and 5 about the ratio of concentration (the ratio of the degree of vacuum in a chamber by the ionization vacuum gage; HMDSO/oxygen) of an example of comparison 6HMDSO steam, and oxygen, and the coat of a silicon oxide was formed for the coat time amount of the oxidation silicon film on the HMDSO polymerization film like the example 7 except 2 minutes and 25 minutes. It was an ellipsometer about the refractive index of the film of the closed-end cylindrical shape-like container which covered these coats, and thickness, and with the weight method, the amount of steam transparency was measured and it was shown in a table 7.

[0040]

[A table 7]

	HMDSO/O ₂ の比率	酸化珪素膜 の被覆時間	酸化珪素膜		二層膜の 水蒸気透過量
			屈折率	膜厚	
比較例 6	0.2	2 分	1.38	180	0.46
	0.2	25 分	1.39	2350	0.14
	5.0	2 分	1.59	190	0.48
	5.0	25 分	1.60	2530	0.25
未被覆					0.49

[0041] (**) unit [of the thickness of the oxidation silicon film]; -- unit;9 of the amount of steam transparency of angstrom and the bilayer film/m² -- day and at 40-degree-C90%RH and [0042]

[Effect of the Invention] Since this invention forms the silicon oxide thin film of the refractive index of the fixed range in the plastics container of a solid configuration by the thickness of homogeneity, the container which was excellent in gas barrier nature can be offered.

[Translation done.]